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MEASUREMENT OF DRY DEPOSITION OF SOx, NOx, NO_2 and O_3

Stocker, D.H, et al.

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Final Report
to the
U.S. Forest Service

Measurement of Dry Deposition of SOx, NOx, NO_2 and O_3

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Under USFS contract No. 28-K6-384

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Summary

Instruments to measure the concentration of NOx, NO_2, and ozone were installed at the Pawnee Grasslands field site (Central Plains Experimental Range) in northern Colorado. The instruments were operated on a continuous basis from December 1986 to February 1987 and from May 1987 to August 1987. These instruments are capable of responding to the rapid changes in concentration associated with changes in the vertical wind velocity. By interfacing these instruments with an anemometer and a computer (supplied by US Forest Service), measurement of the flux of NOx, NO_2 and ozone was possible. To ensure data quality the system was automatically zeroed at the end of each half hour sampling interval and calibrated manually on a weekly basis. Initial results indicate that the system was operating correctly.

The SOx analyzer is currently undergoing further development in the laboratory to improve sensitivity and speed of response.

Introduction

The flux of a reactive gas is both species as well as surface dependent (Sehmel, 1980 and Voldner et al., 1986), hence measurements over many types of surface are needed for each species. The flux of any species is the product of the the of concentration c_a, and vertical wind velocity w;

$$F = c_a w$$

The concentration and the vertical wind velocity at any instant can be expressed as the sum of an average component and a fluctuation about the mean, the average flux is then,

$$\overline{F} = \overline{(\overline{c_a} + c_a').(\overline{w} + w')}$$

Since the net vertical transport of air is set to zero for the sampling period by coordinate rotation, the average vertical wind speed is also zero, if the effects of varying air density are ignored, the average flux then becomes,

$$\overline{F} = \overline{c_a' w'}$$

This equation forms the basis for the eddy correlation technique. The deviations of the concentration and vertical wind velocity from their mean values are correlated to give a direct determination of the flux without the need for inferred quantities such as eddy diffusivities (Hicks et al., 1980 and Hicks, 1986). However, the technique requires the deployment of fast response ($\geq$1 Hz) sensitive instruments. Chemiluminescent detectors are capable of rapidly responding to the small changes in concentration, required for Eddy Correlation studies (Stedman, 1985). The Phillipson Research Group has contributed significantly to

the design and construction of such instruments.

This research project was designed to measure the dry deposition of NO_2, NOx (principally NO + NO_2 + peroxyacetyl nitrate (PAN)) and ozone to grassland during winter and summer months. Working with the US Forest Service in Fort Collins who provided the shelter, tower, meteorological measurements and data acquisition system, our task was to provide the chemical analysis. This included the installation, operation and maintenance of the intake system, detectors and the zero and calibration system.

Experimental

The field site was on the Central Plains Experimental Range about 7 miles north of Nunn in northern Colorado. An air conditioned shelter and meteorological tower were provided by the US Forest Service in Fort Collins.

The field setup was the result of a compromise between chemical and meteorological requirements. The sensors should be placed sufficiently high on the tower such that the eddies observed are large enough for the response speeds of the instruments, yet not so high that the fetch is no longer adequate or the flux measured is unrepresentative of the flux at the surface. The chemical sensors need to be as close as possible to the anemometer, but far enough away so that steady-state wind flows are maintained.

A Gill u,v,w propeller anemometer was positioned at a height of 5m on the tower which was 30^{o} northeast of the

shelter and 20.5m distant. Our instruments were housed in the shelter and air was brought from the tower to the shelter using a high volume sample pump. The arrangement avoided introducing extraneous turbulence to the mean wind flow and kept the instruments in a temperature controlled environment.

The intake system consisted of a 26.5m long, 5/8 inch i.d. Telfon tube through which air was drawn at ca. 160 lpm using a high volume air pump (Fuji ring compressor). The flow rate decreased with time, see table 1. The intake was in the uv plane of the anemometer ca. 3 inches from the spine of the anemometer. The chemical sensors sampled from the main air stream and returned their exhaust downstream of the sampling manifold to keep the pressure drop across the instruments to a minimum. Figure 1. shows a block diagram of the field installation. The time taken for a sample to reach the detectors from the tower was ca. 2 seconds. Adjustment for this delay was incorporated in the data collection and reduction routines (McMillen, 1986). The sample tube dampened the response of the chemical sensors to rapid (>1Hz) changes in concentration. This arose from the adsorption/desorption of gases on the walls of the sample tube and the turbulent flow conditions ($Re > 2 \times 10^7$) which led to a slight mixing of the gas samples. Thus a smearing of the high frequency changes in concentration occurred. The interference caused by adsorption/desorption was minimized by using large bore Teflon tubing. Although the length of

sample tube slowed the response of the chemical instruments and cut off the high frequency flux data, the need for a complex temperature correction was eliminated by housing the instruments in a temperature controlled shelter. Some of the high frequency data "lost" can be retrieved using suitable algorithms (Moore, 1986).

Table 2 presents a summary of the chemical instruments and their specifications.

Chemiluminescent Ambient Air Monitors (CAAM)

The same instrument design can be adapted to measure nitrogen dioxide (Wendel et al., 1983)and ozone (Ray et al., 1986) by changing the fluorescent reagent used.

The sample flowed through a detection cell and over a filter pad wetted with the fluorescent reagent, see Figure 2. A blue sensitive photomultiplier tube monitored the light produced. The fluid and air exited at the bottom of the reaction cell and were separated by gravity in the catch reservoir. The fluid flow rate was 1 ml/min and the air flow rate was 10 lpm. The response of these instruments was pressure dependent.

For the detection of nitrogen dioxide a basic solution of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) was used (Maeda et al., 1980). The solution was comprised of 0.05 M NaOH, 0.1 M Na_2SO_3, 2×10^{-4} M luminol and 0.05% v/v t-butanol. The solution was used once and then discarded. Operating under these conditions the sensitivity was ca. 0.2 μA/ppb (parts per billion volumetric mixing

ratio) and the response was linear from 0.1 ppb, see Figure 3. The response of the instrument did decay with time after a fresh solution was installed and the filter pad in the detection cell changed, this was probably due to degradation of the filter pad and aging of the solution. The solution was replaced approximately weekly and the instrument recalibrated, see table 1. for details of the calibration changes. When operated in the laboratory the instrument responded to a square wave pulse of NO_2 introduced to the intake of the instrument within 0.2 seconds. Under field conditions, the response to a square wave pulse of clean air introduced to the system at the tower was slower (0.7s) because broadening of the sample occurred in the intake system, see Figure 4. The detection limit was 0.14 ppb.

For the analysis of ozone the basic luminol solution was exchanged for a solution of Eosin-Y in ethylene glycol. The dye solution was recycled after each batch had passed through the instrument. The ozone detector was calibrated by comparing the output signal with that from a slow response UV photometric ozone monitor (TECO model 49A). The sensitivity was 0.12 μA/ppb and the detection limit was < 1 ppb in the field. In the laboratory the response of the instrument was 7 Hz, which decreased under field conditions to 1.4 Hz due to the broadening which occurred when sampling through the long intake tube, see Figure 5.

Total NOx Analyzer

NO reacts with ozone forming electronically excited nitrogen dioxide. At reduced pressure the excited nitrogen dioxide decays to the ground state emitting a photon;

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + h\nu \quad (640\ nm)$$

The intensity of light produced is proportional to the concentration of NO, forming the basis for the total NOx analyzer (Fontijn, 1970).

The higher oxides of nitrogen were reduced to NO by passing the sample gas through a hot molybdenum converter at 400°C. The principle species reduced were NO_2 and peroxyacetyl nitrate (PAN) (Dickerson et al., 1984). Nitric acid is known to pass through the length of the sample tubes to reach the converter which was housed in the shelter, but has been shown in the past to have a response time larger than 120s. This slow response is presumed to arise from a "chromatographic" effect of HNO_3 sticking and releasing from the intake tubing. The response time for nitric acid is too slow to allow correlation with changes in vertical wind velocities to determine HNO_3 fluxes.

The reduced sample gas was mixed with excess ozone prior to entering the reaction chamber in front of a cooled red sensitive photomultiplier tube (EMI 9658). The walls of the reaction chamber were gold plated to enhance reflectivity and provide an inert surface. Ozone was produced by passing 250 ml/min of O_2 through three parallel

discharge tubes, a water bubbler in the ozone line decreases the background signal (Drummond and Voltz, 1982). The analyzer is shown schematically in Figure 6. The photomultiplier tube output was fed to a programmable electrometer (Keithley 18000-20).

The instrument was operated with a chamber vacuum of 5-10 torr and a sample flow rate of approximately 4 lpm. Under these conditions the instrument response was ca. 0.3 nA/ppb with background noise equivalent to a detection limit of ca. 0.07-0.2 ppb, however, at times the noise was greater than this. The sensitivity of the instrument was constant throughout each experimental period, as shown in table 1. The change in sensitivity between the two experimental periods was due to a fault in the electrometer. The instrument was less sensitive when ambient air was used for ozone generation, which was necessary when the oxygen cylinder had emptied. The response of the analyzer to NO_2 was linear until the signal to noise ratio approached unity, see Figure 3. When operated in the laboratory the instrument responded to a square wave pulse of 10 ppb of NO within 0.3s, see Figure 7. However, when operated in the field and sampling through the long intake tube, the response was somewhat slower at 0.9s.

Experiments carried out by heating the intake gases to the analyzer while keeping the concentration of span gas constant showed no deviation in response, therefore the response of the instrument was not pressure dependent. This

is consistent with the conclusions of Steffenson et al., 1974, provided constant volume vacuum pumps are used.

Flame Photometric Sulfur Analyzer

This is a total sulfur analyzer (SOx). Sulfur compounds are determined by burning the sample gas in a hydrogen rich flame (Hadjitofi and Wilson, 1979). The S atoms produced recombine to form sulfur molecules in an excited state. These excited sulfur molecules decay to the ground state emitting a photon of wavelength 394 nm (Sugiyama et al., 1973);

$$SOx \longrightarrow H_2S$$

$$H_2S + H \longrightarrow HS + H_2$$

$$HS + H \longrightarrow S + H_2$$

$$S + S + M \longrightarrow S_2^* + M$$

$$S_2^* \longrightarrow S_2 + h\nu$$

where M is a third body.

This instrument is currently undergoing further development and testing in the laboratory. The detection limit is ca. 1 ppb, however, possible interferences from the presence of water vapor, carbon dioxide and pressure effects need to eliminated.

Zero and Calibration Systems

The instruments used in this study are highly sensitive and consequently are susceptible to some base line drift, thus it is necessary to keep track of the response of these instruments to clean, unpolluted air.

"Zero air" was prepared by scrubbing ambient air using a series of traps. The first contained ferrous sulphate which reduced NO_2 to NO which was then removed by a second trap filled with Purafil. A third trap filled with activated charcoal removed ozone. A compressor was used to fill a 30 gallon tank to a pressure of 100 psi with zero air. At the end of each sampling period zero air was introduced at the inlet to the main sample line through 3/8 inch i.d. black Teflon tubing. The flow of air to the tower intake, ca. 170 lpm, was sufficient to over-vent the main sample flow at a constant flow rate for approximately three minutes

The system was calibrated on a weekly basis. This was achieved by adding a known flow of span gas to the zero air supply while the zero air flow rate was still constant. The NOx analyzer was calibrated using a span gas mixture of 10 ppm NO in N_2. The NO_2 CAAM instrument was calibrated using a 1000 ppm NO_2 in N_2 standard, the concentration of NO_2 reaching the instruments was checked against the NOx analyzer.

Data Analysis

Data collected during periods of calibration or when the sample collection period was too short (<20 minutes) should be rejected. Protocols used previously for filtering poor data points include analysis of the wind direction, if the fetch was over the trailer and through the tower data should be discarded since both act as sources of anomalous turbulent flow. Data obtained under non-steady-state

conditions was also discarded, i.e. when there were rapid changes in concentration or wind direction. To identify these points the roughness length (z_o) was calculated from the logarithmic wind law which assumes neutral conditions.

$$\frac{k\bar{u}}{u_*} = \ln \frac{z}{z_o}$$

where k is the vonKarman constant (0.4), u the wind velocity, u_* the friction velocity and z the height of the anemometer. Although the conditions were not always neutral, for the purposes used here, the neutral roughness length is a useful tool to indicate the occurrence of non-steady-state flow patterns. Figure 8. shows an example of the data collected over a wheat field at Bennett Colorado, in which the roughness length is plotted as a function of wind direction. In Bennett the anemometer was situated to the south of the tower and trailer, wind directions between 300^o and 90^o were discarded since they consistently give rise to neutral roughness lengths greater than 1m (Evilsizor et al., 1987). Chemical non-steady-state conditions can be identified by large variance in the half hour averaged concentrations, see Figure 9. for an example from a field study carried out downwind of a major source of pollution in an otherwise clean environment. Periods of plume impaction at ca. 10:00 hrs are clearly visible as are rapid changes in concentration brought about by changes in wind direction. Data obtained between the times 6:00 to 8:30 and 18:00 to 21:30 were not included in the final calculation of the

average fluxes measured at this site. These times correspond to sunrise and sunset respectively as the change is made from downslope drainage winds to convective mixing in the valley bringing the pollution plume to the site (Stocker et al., 1987). Finally data points lying outside 3 standard deviations of the mean flux taken over a five day period were rejected as being statistically insignificant i.e. they lie outside the 99.7% confidence interval.

Any remaining data points were averaged. One treatment involved a five-channel smoothing routine using the coefficients from the binomial expansion,

$$Y'_{(x)} = \frac{1}{9}Y_{(x-2)} + \frac{2}{9}Y_{(x-1)} + \frac{1}{3}Y_{(x)} + \frac{2}{9}Y_{(x+1)} + \frac{1}{9}Y_{(x+2)}$$

where $Y_{(x)}$ represents the magnitude of the x^{th} sampling interval. Another method for smoothing the data involved averaging the data for each half hour interval over several days, to build a picture of an average day. The number of days over which the data was averaged varied from 5 to 25, depending on the prevailing conditions. An analysis of variance will reveal real flux trends which may be buried in the noise. (Spiegel, 1975).

Correction has to be applied to the data if the response of the chemical sensors is pressure dependent i.e. the instruments respond to changes in density (g/cm^3) rather than the mixing ratio (ppb) (Webb et al., 1980 and Businger, 1986). This correction will be necessary for the data collected using the CAAM instruments.

Future Work

The performance in eddy correlation studies of a sonic anemometer should be compared with that of a propeller anemometer (eg. the Gill uvw anemometer used in this study). This would aid in the interpretation of the results obtained from this study and other previous work.

As soon as the SOx analyzer is functioning in a reliable and predictable mode, field measurements of the flux of SOx to prairie grassland and snow should be performed. Other chemical measurements of interest include the measurement of the flux of NOy ($NOx + HNO_3$) using a new intake system (currently under development) for the chemiluminescent NOx analyzer used in this study. The NOx analyzer in it's present configuration is capable of measuring the flux of NO, this along with the concentration of PAN (using a chromatographic technique should be measured to determine a nitrogen flux budget. The concentration of PAN can be determined using a chromatographic technique developed in these laboratories based on a luminol detector (Burkhardt et al., 1987).

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Table 1. Calibration data for the chemical sensors operated at the Pawnee Grasslands field site.

Date	Julian Date	Flow Rate[a]	Ozone[bc]	NO_2[c]	NOx[d]
				ppb/V	ppb/V
11-Dec	345	178	Fresh	11.1[e]	3.13
12-Dec	346				
13-Dec	347				
14-Dec	348				
15-Dec	349				
16-Dec	350				
17-Dec	351			3.2	2.78[f]
18-Dec	352				
19-Dec	353		15:55		
20-Dec	354				
21-Dec	355				
22-Dec	356			2.53 3.92[e]	
23-Dec	357				
24-Dec	358		13:10		
25-Dec	359				
26-Dec	360				
27-Dec	361				
28-Dec	362				
29-Dec	363		Recycled		
30-Dec	364				
31-Dec	365			e,g	
1-Jan	1				
2-Jan	2		11:45		
3-Jan	3				
4-Jan	4				
5-Jan	5				
6-Jan	6				
7-Jan	7		Recycled		
8-Jan	8		h	2.13 21.3[i]	2.77
9-Jan	9				
10-Jan	10				
11-Jan	11				
12-Jan	12		Recycled		
13-Jan	13				
14-Jan	14				
15-Jan	15				
16-Jan	16		Recycled		
17-Jan	17				
18-Jan	18				
19-Jan	19				
20-Jan	20		Recycled	29.4	3.27
21-Jan	21			e	
22-Jan	22				

Date	Julian Date	Flow Rate[a]	Ozone[bc]	NO_2[c] ppb/V	NOx[d] ppb/V
23-Jan	23				
24-Jan	24			e?	
25-Jan	25				
26-Jan	26				
27-Jan	27	j	k	44.7	3.21
28-Jan	28				
29-Jan	29		Recycled		
30-Jan	30				
31-Jan	31				
1-Feb	32				
2-Feb	33	End of winter experiment.			

Date	Julian Date	Flow Rate[a]	Ozone[bc]	NO_2[c] ppb/V	NOx[dl] ppb/V
13-May	133		Fresh	e	
14-May	134	159		10.0	0.038
15-May	135				
16-May	136				
17-May	137				
18-May	138		11:45	15.7[m] 12.1[e]	0.034
19-May	139				
20-May	140				
21-May	141		12:30	3.13[e,h,n,o]	0.034[p]
22-May	142			o	
23-May	143			2.1[e,n]	
24-May	144		refill(am)		
25-May	145				
26-May	146			1.079[e,n,o,q]	
27-May	147			3.92	0.04
28-May	148				
29-May	149		12:25		
30-May	150				
31-May	151				
1-Jun	152	158	r	7.41	
2-Jun	153		r		
3-Jun	154				
4-Jun	155				
5-Jun	156		9:05	1.56[e,m,n]	
6-Jun	157				
7-Jun	158				
8-Jun	159			s	t
9-Jun	160				u

Date	Julian Date	Flow Rate[a]	Ozone[bc]	NO_2[c] ppb/V	NOx[d] ppb/V
				4.39[e]	
11-Jun	162		8:46		
12-Jun	163				
13-Jun	164				
14-Jun	165				
15-Jun	166		11:00		
16-Jun	167			7.83	0.083[p]
17-Jun	168				
18-Jun	169		k	7.98	0.039
19-Jun	170				
20-Jun	171				
21-Jun	172				
22-Jun	173		7:48		
23-Jun	174	158[v]		h,k	
24-Jun	175	164			
25-Jun	176				
26-Jun	177				
27-Jun	178				
28-Jun	179				
29-Jun	180				
30-Jun	181	162	6:40[w]	8.98	0.048[p,x]
1-Jul	182				
2-Jul	183			6.14	0.029
3-Jul	184				
4-Jul	185			y	
5-Jul	186				
6-Jul	187		7:48		0.031[p]
7-Jul	188			3.67[e,k]	
8-Jul	189				
9-Jul	190				
10-Jul	191			17.7 2.71[h]	0.051
11-Jul	192				
12-Jul	193				
13-Jul	194		6:47		
14-Jul	195				
15-Jul	196	z		6.33	0.038
16-Jul	197	aa			
17-Jul	198				
18-Jul	199				
19-Jul	200				
20-Jul	201		11:30		
21-Jul	202				
22-Jul	203				
23-Jul	204				
24-Jul	205				
25-Jul	206				
26-Jul	207				
27-Jul	208	Site shutdown			

a; Measured using a dry gas meter attached to the exhaust of the large sample pump, correcting for the flow through the NOx analyzer which is not returned to the sample inlet.

b; Wherever possible the times when the dye solution was recycled is reported.

c; The calibration factor is in units of ppb/V, the calibrated sensitivity in parts per billion mixing ratio per volt observed by the data acquisition system when the instrument is working with a full scale deflection of 10 μA.

d; 10 nA full scale deflection.

e; Fresh solution.

f; Converter heater repaired.

g; Solution changed, but neither old nor new solutions calibrated.

h; Change target pad.

i; Changed full scale deflection to 100 uA.

j; Change zero air traps.

k; Air pump replaced.

l; Response of NO_x analyzer has changed by a factor of 100 which implies an electronic rather than a chemical fault is to blame. The response of the NO_x analyzer is also very noisy.

m; Luminol flow stopped.

n; No calibration of old solution.

o; No luminol left.

p; Oxygen tank empty.

q; High calibration, signal may not have stabilized.

r; TECO photometric ozone monitor recalibrated.

s; No calibration possible as NO_x analyzer off line.

t; Plugged frit in ozone line.

u; Repair of ozone generator in DU laboratories.

v; Change air filters in main sample line, system is off line.

w;Reservoir dry before refill.

x; Plugged sample intake.

y; Broken air pump.

z; Zero air system self destructs, trap explodes.

aa; Replace zero air trap.

Table 2. Summary of the characteristics of the chemical sensors used during the field study.

Chemical Measured	Instrument Name	Principle	Detection Limits	Sensitivity	Comments
Total NOx	NOx Box	Chemi-luminescence	0.1 ppb -1000 ppm	0.3 uA/ppb	Requires high pressure O_2 cylinders for O_3 production; large vacuum pumps; cooled red sensitive pmt; high power (240v). Fast response < 1 sec NOx by catalytic reduction using Mo turnings at 400°C. Stable calibration.
NO_2	CAAM 2	Chemi-luminescence	0.1 ppb -30 ppm	0.2 μA/ppb	Uses a basic luminol solution which cannot be recycled. Each batch of reagent requires calibration. Sensitivity of solution decreases with time. Calibrate and check target pad weekly. < 1 sec response time. Portable low power required.
Ozone	Teco Model 49	uv absorption	1 ppb - 1 ppm	0.2mv/ppb	EPA standard. Slow response.
Ozone	CAAM 1	Chemi-luminescence	0.1 ppb -400 ppb	0.12 μA/ppb	Uses Eosin-Y in Ethylene Glycol which can be recycled but some sensitivity is lost with use. < 1 sec response time. Calibrate using uv photometric instrument. Period of unattended use limited by reservoir size. Target pad checked weekly. Portable low power required.

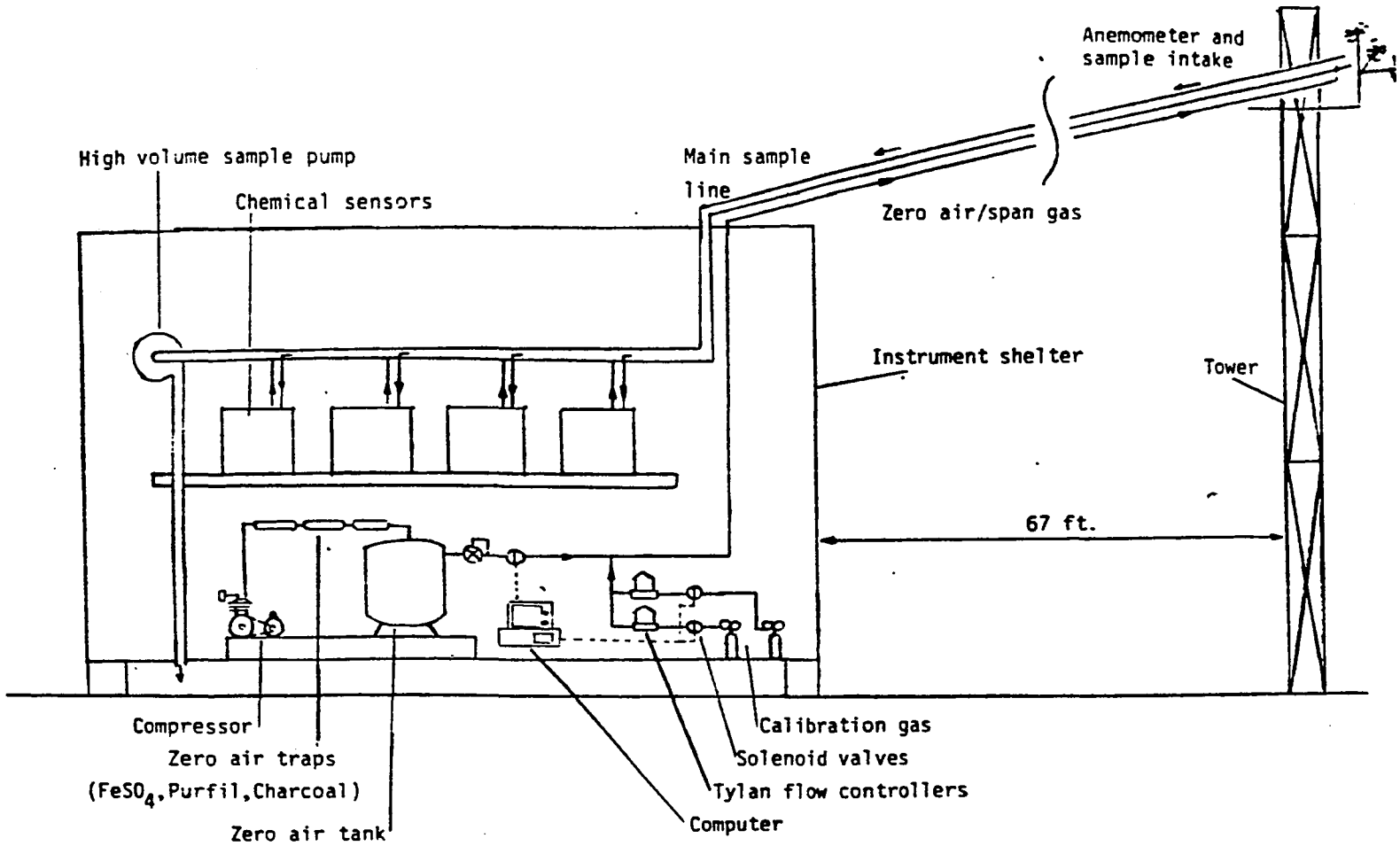
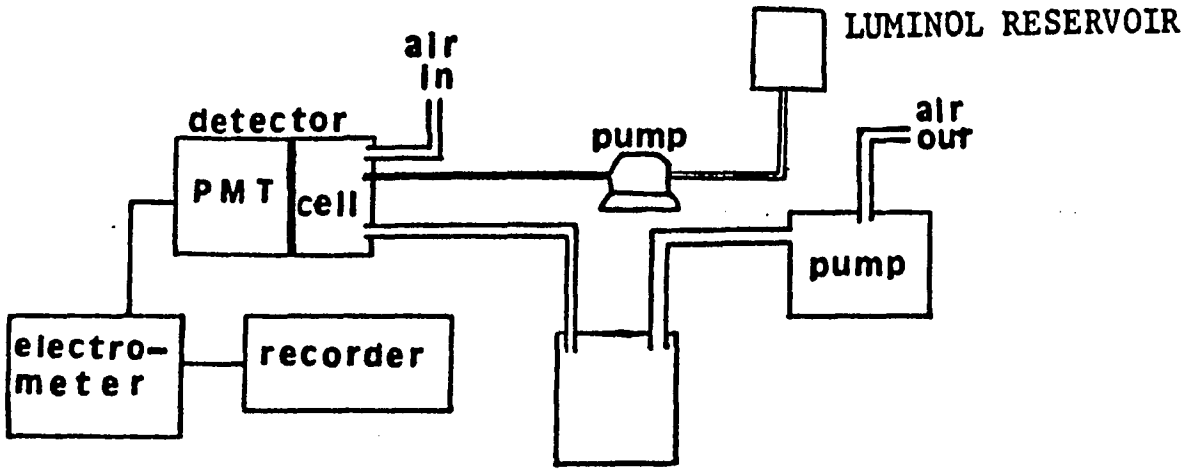


Figure 1. Schematic diagram of the installation of the chemical instruments at the field site.



DETECTION CELL DESIGN

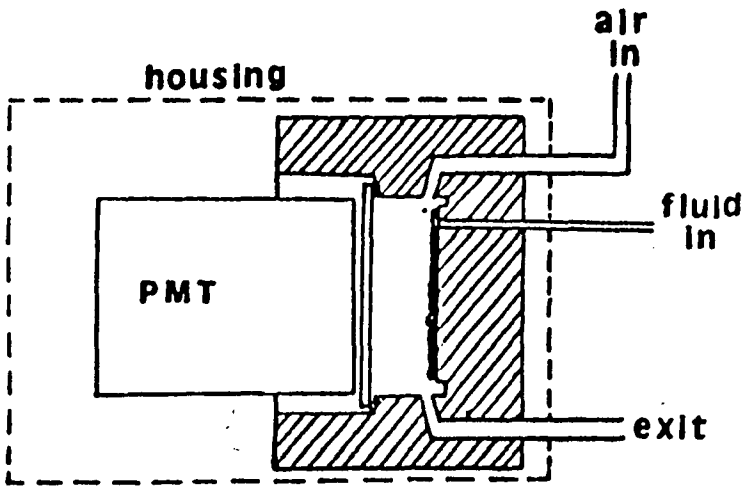
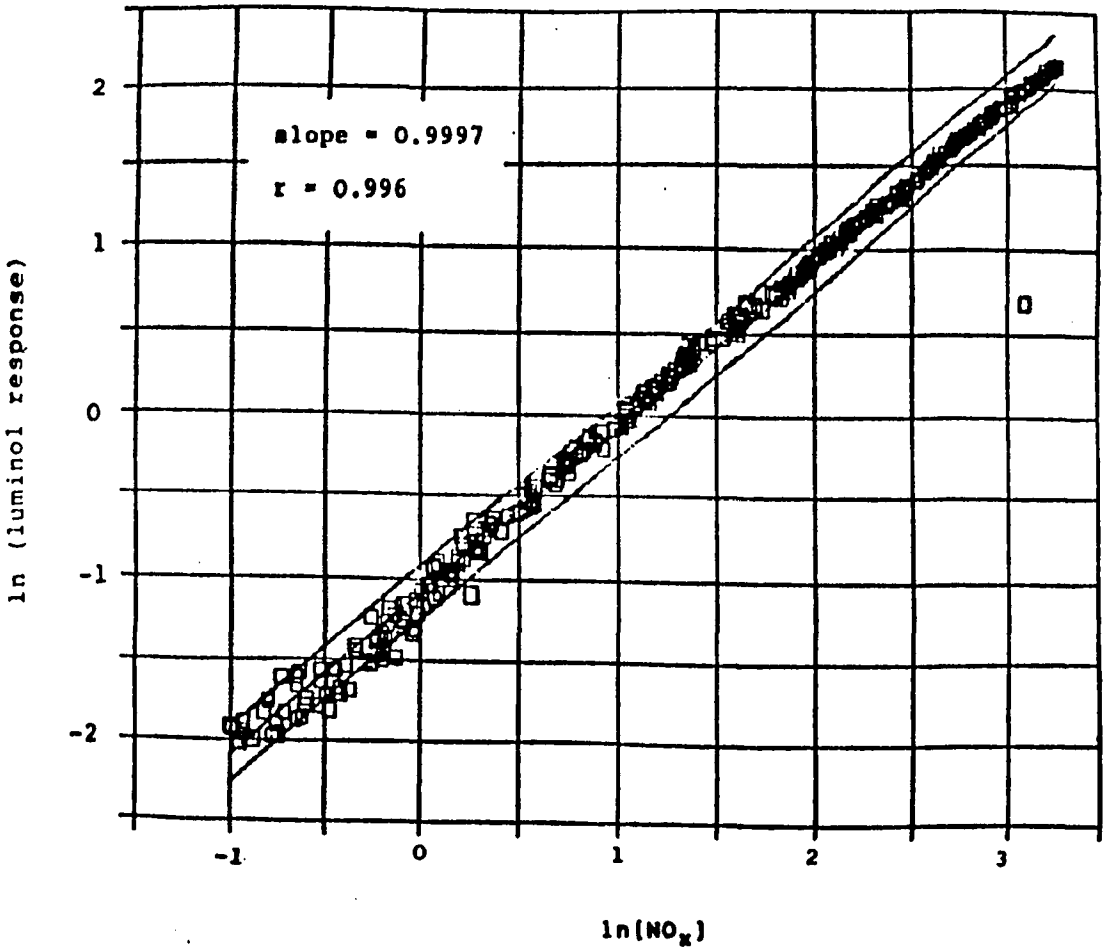


Figure 2. Schematic diagram of the Chemiluminescent Ambient Air Monitor with the design of the detection cell which is machined from black Delrin, a glass window seals the cell.



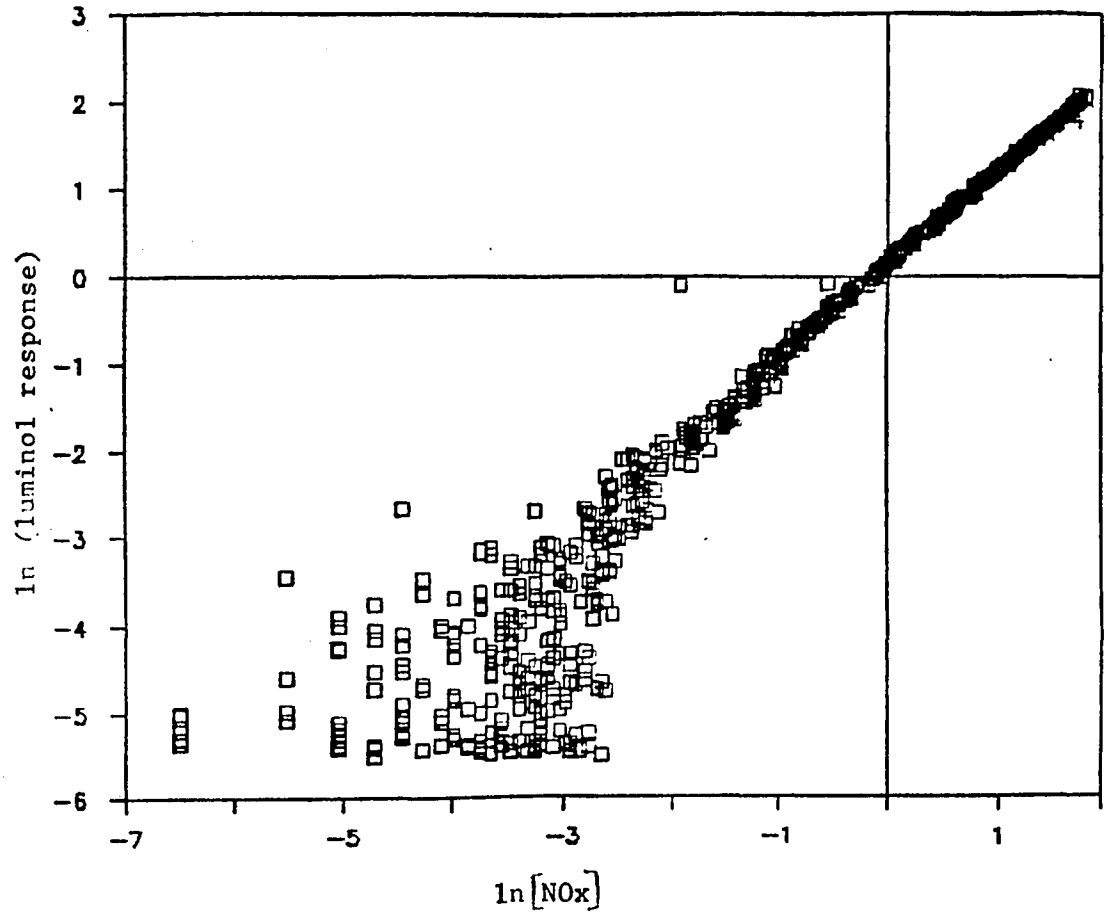
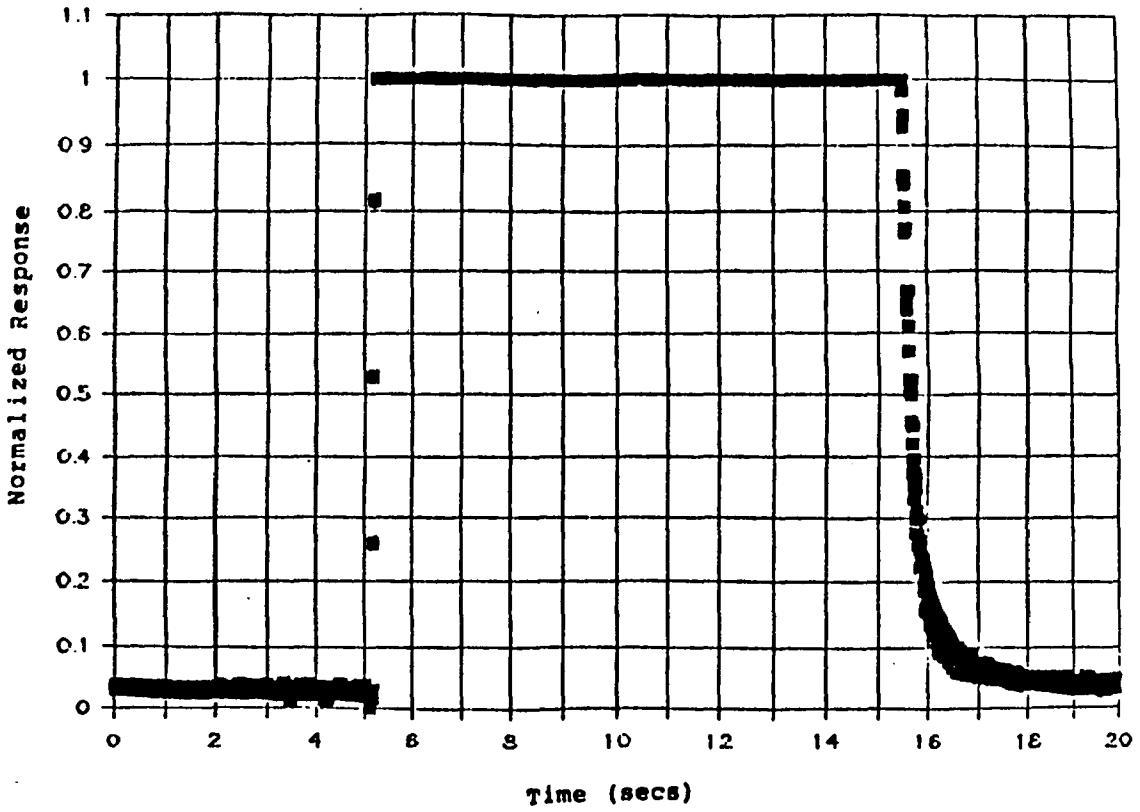


Figure 3. The response of the total nitrogen oxides detector and the nitrogen dioxide detector to low concentrations of nitrogen dioxide.



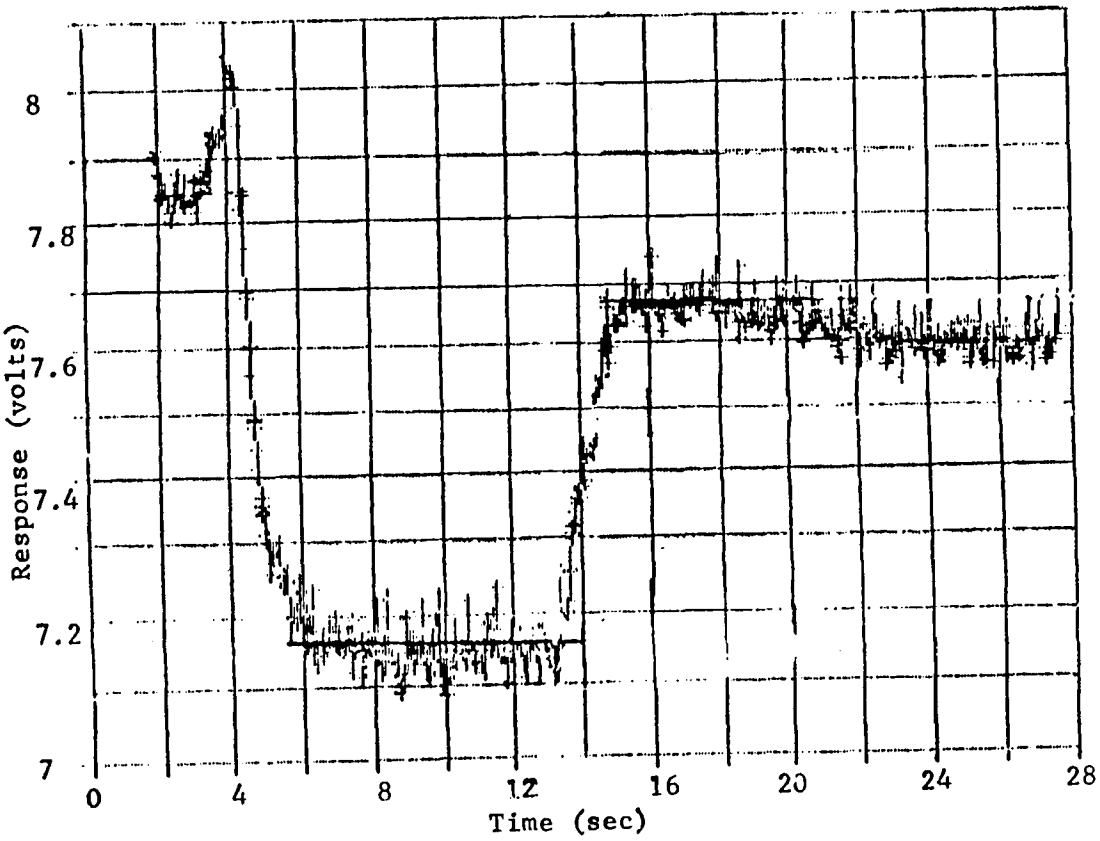
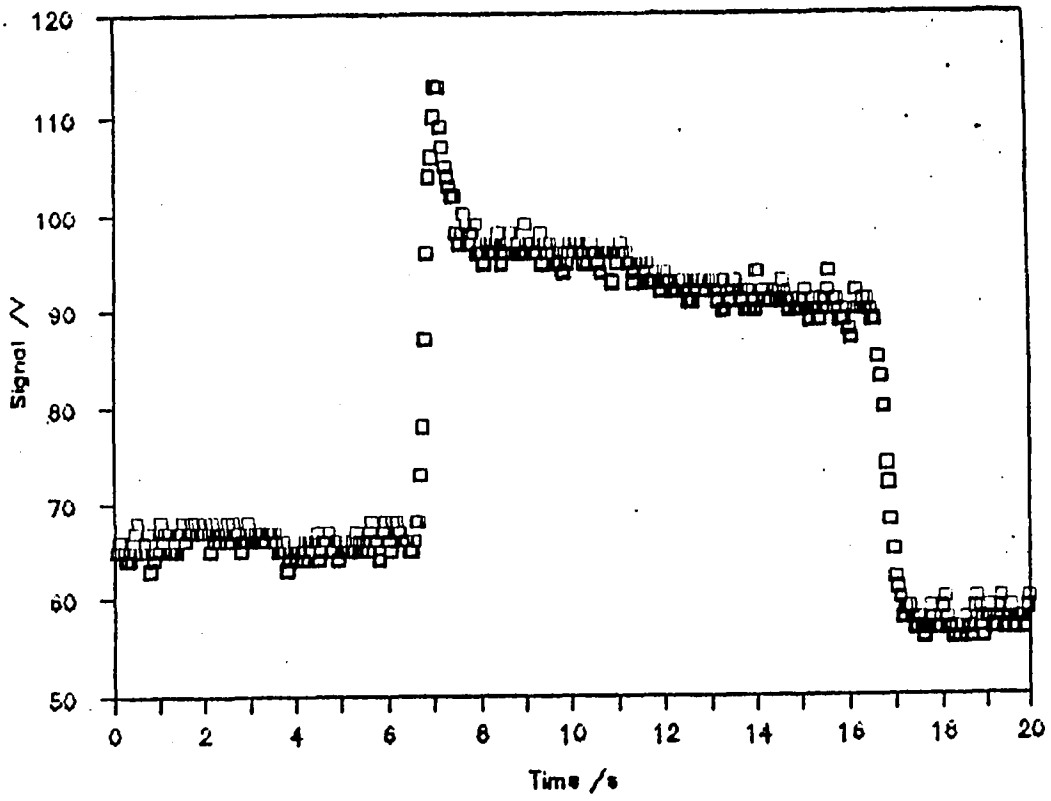


Figure 4. Frequency response of the nitrogen dioxide detector; (a) to a square wave pulse of nitrogen dioxide in the laboratory and (b) to a square wave pulse of zero air operating in the field introduced at the inlet on the tower.



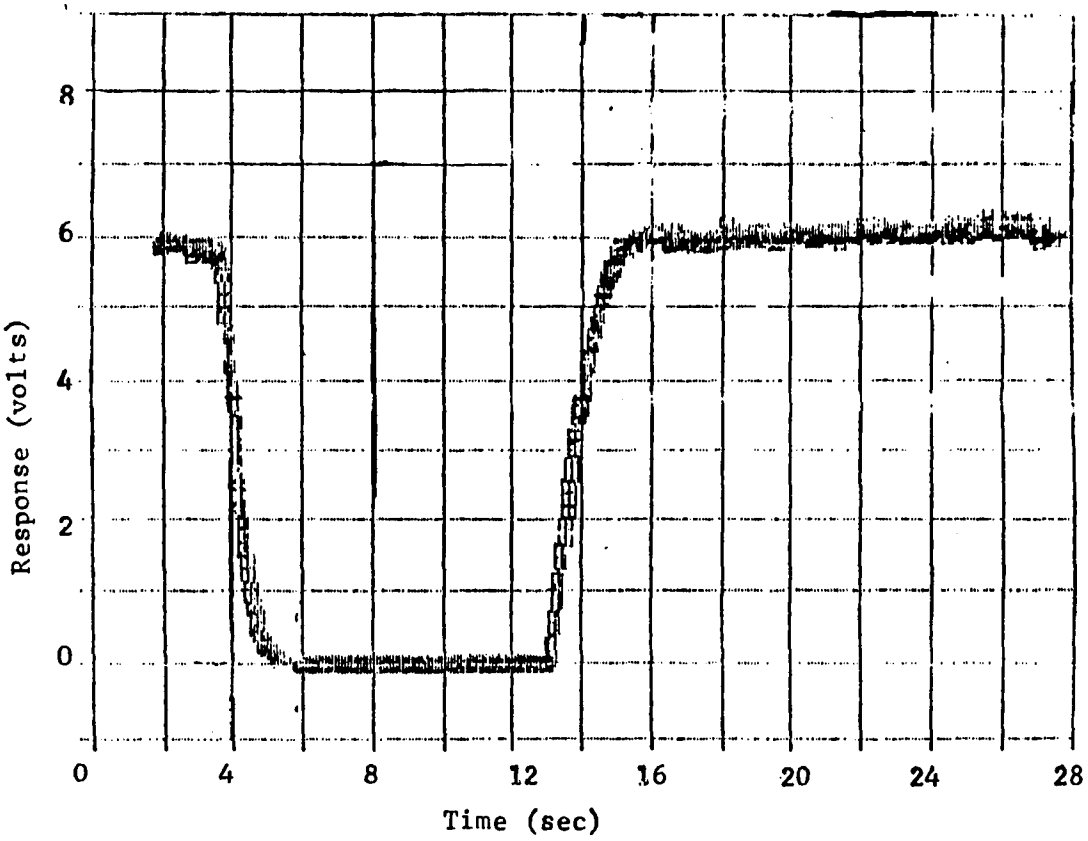


Figure 5. Frequency response of the ozone detector; (a) to a square wave pulse of ozone in the laboratory and (b) to a square wave pulse of zero air operating in the field introduced at the inlet on the tower.

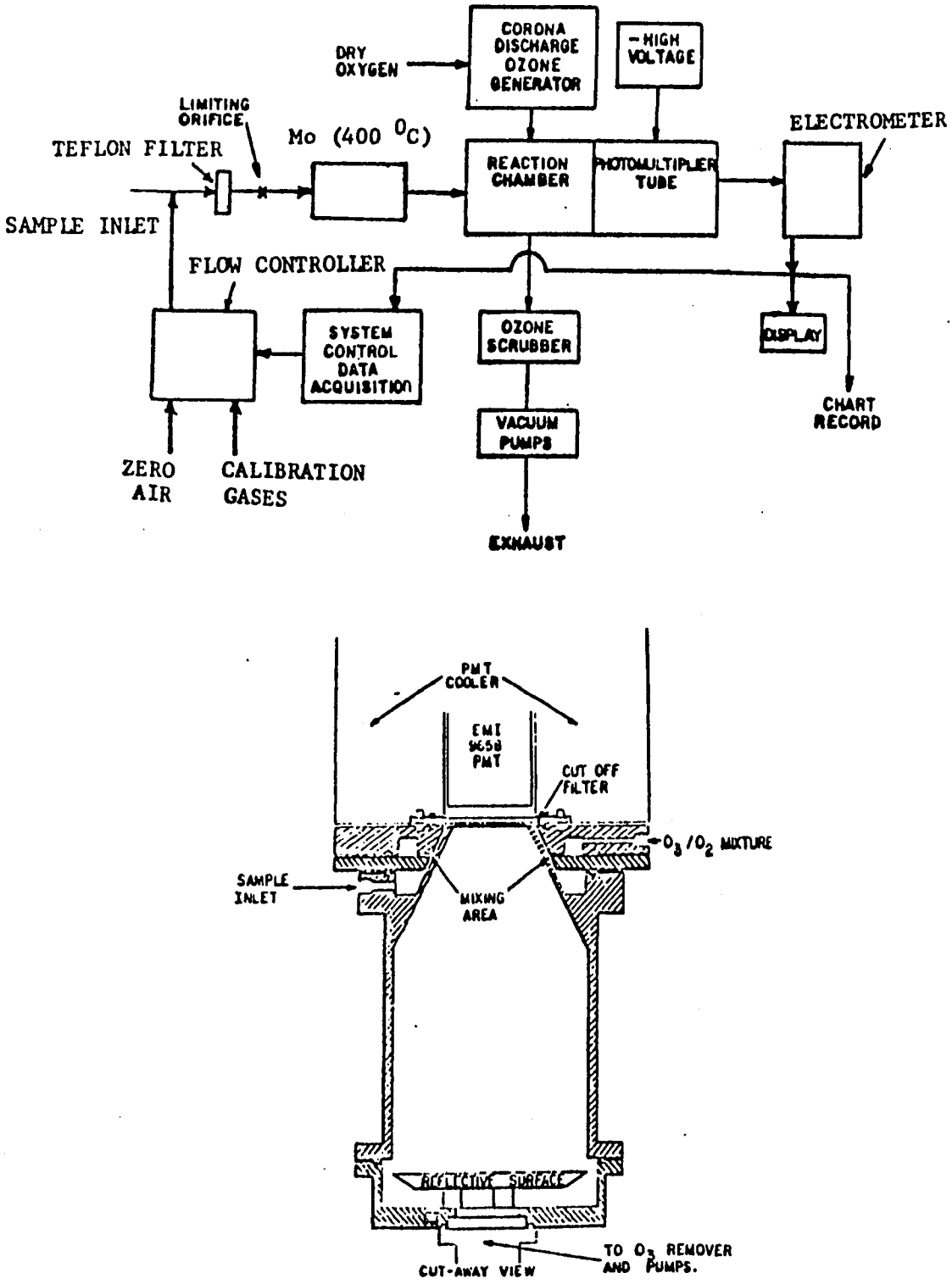


Figure 6. Schematic diagram of the total oxides of nitrogen detector with a sectional view of the reaction chamber.

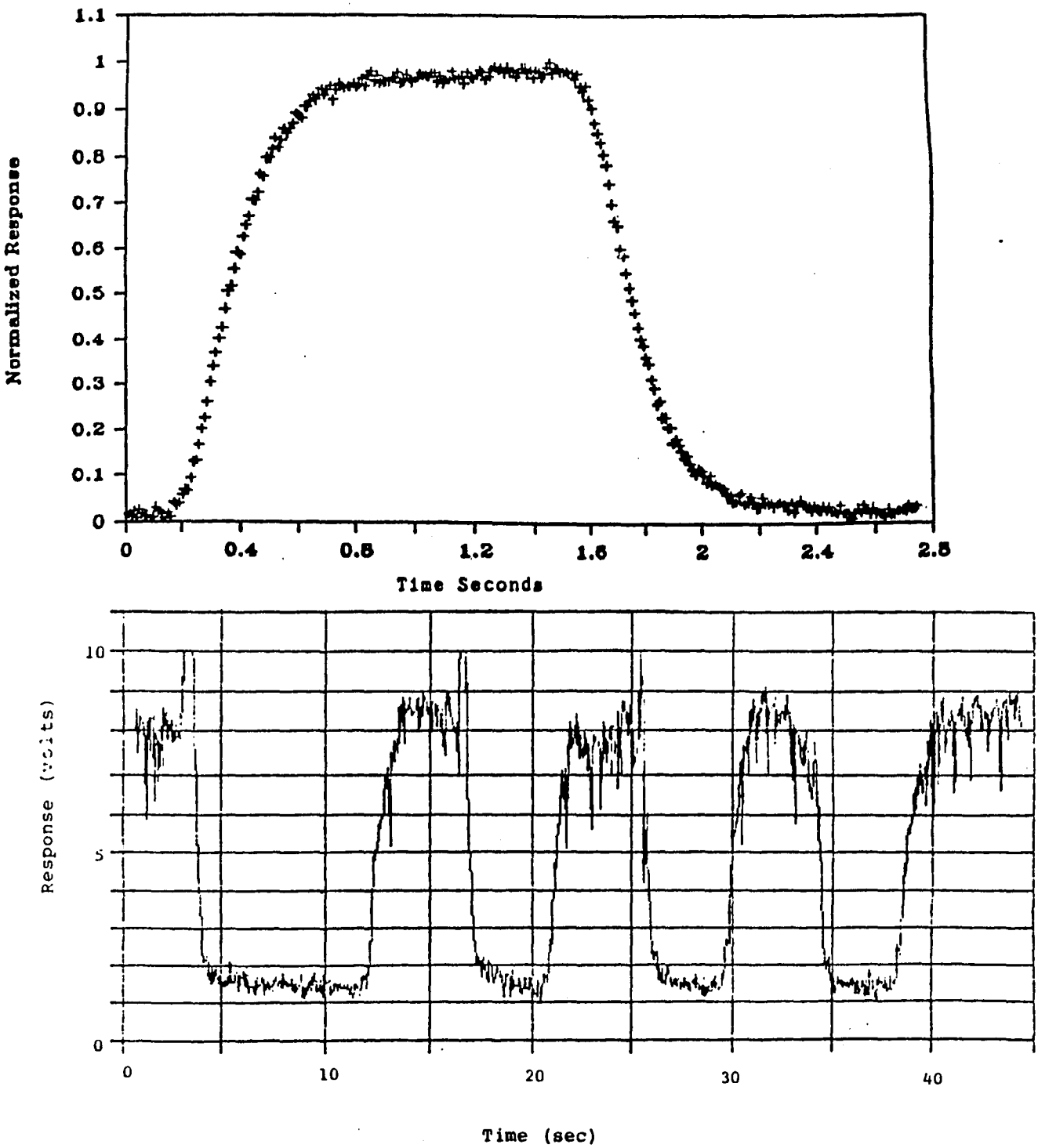


Figure 7 Frequency response of the total NOx analyzer (a) to a square wave pulse of 10 ppb NO in the laboratory and (b) to a square wave pulse of zero air introduced to the tower inlet in the field.

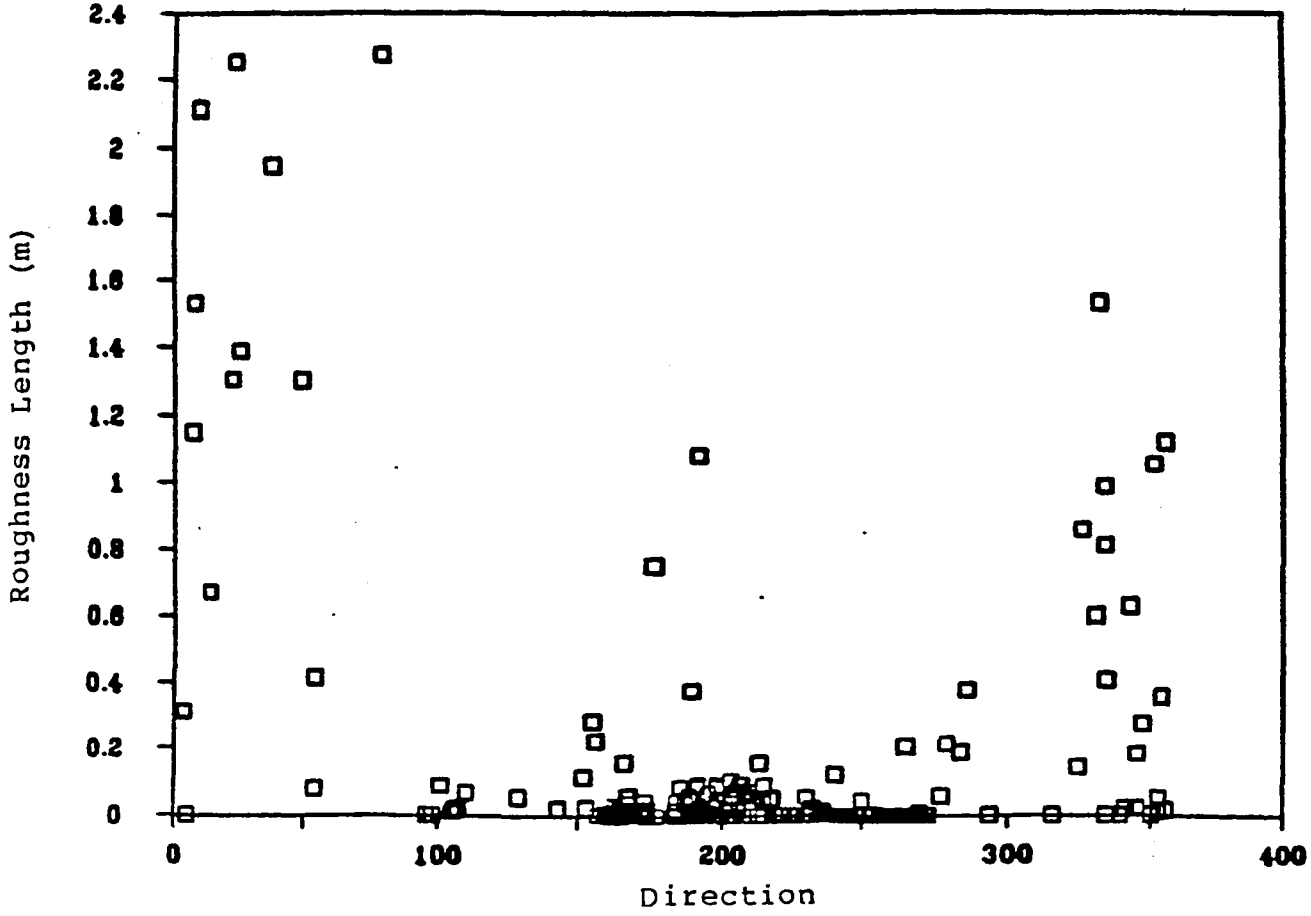


Figure 8. The variation of the roughness length assuming neutral conditions with wind direction at the Bennett field site. Data collected from 16 Feb. to 20 Feb. 1986.

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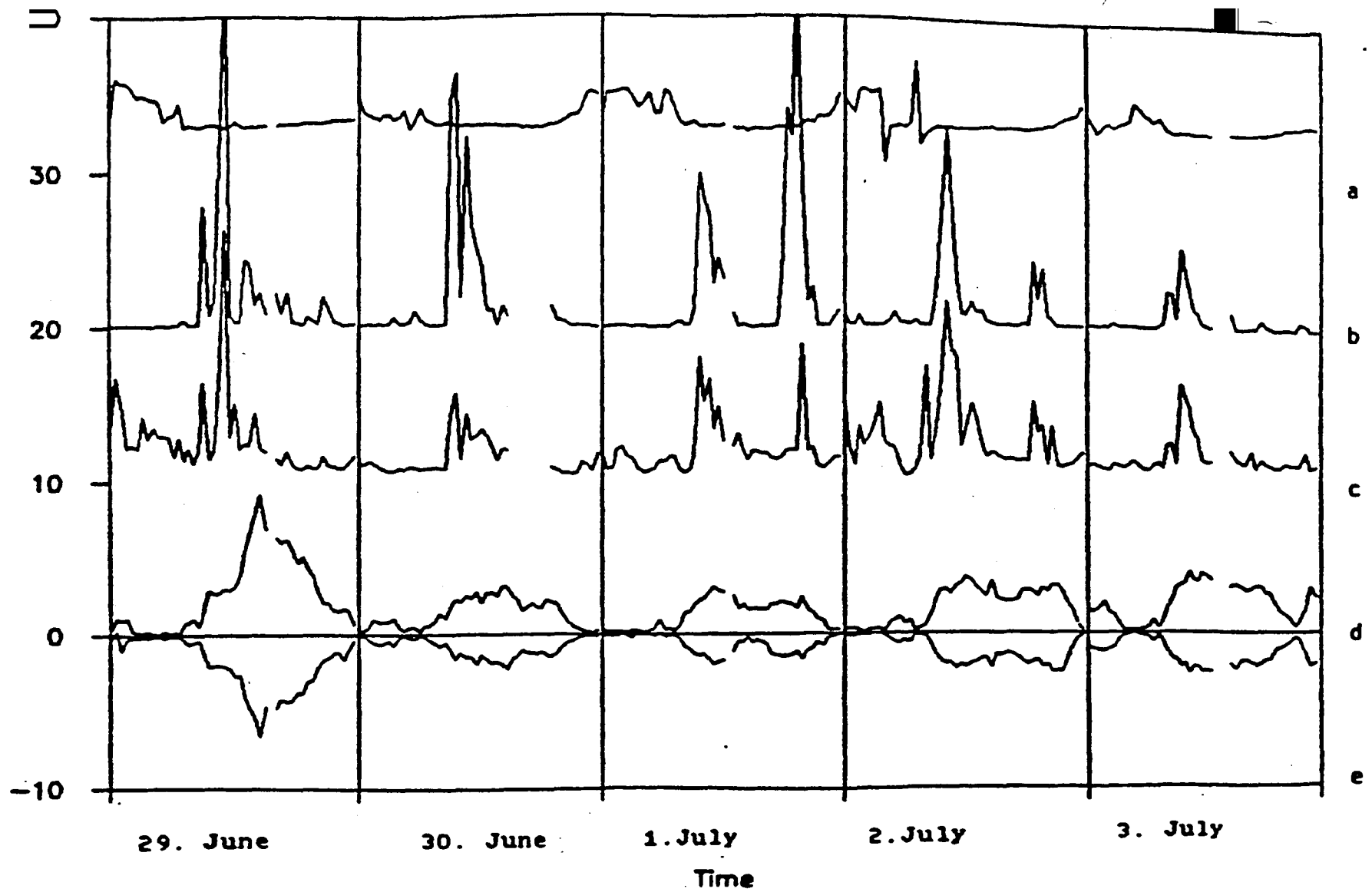

Figure 9. A comparison of the variance of the concentrations of NO_2 {$(ppb^2/10) + 20$} (b) and ozone {$(ppb^2/10) + 10$} (c) with the variance of the vertical wind velocity $\overline{w'^2}$ (m^2/s^2) (d), $\overline{w'u'}$ (m^2/s^2) (e) and the wind direction θ (a) {$(\theta/50) + 30$} as a function of time for the period 29 June to 3 July 1986 at a desert field site.